

# Long-Term Trends of Trace Gases over Mauna Loa

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## INTRODUCTION

Since November 1991, the University of Denver (DU) has operated a very high resolution ( $\sim 0.0035 \text{ cm}^{-1}$ ) Fourier transform spectrometer (FTS) from the Network for the Detection of Stratospheric Change (NDSC) site at Mauna Loa Observatory to obtain atmospheric transmission spectra in the infrared region of the solar electromagnetic spectrum. Initially, a Bomem DA3.002 FTS was employed. This instrument required considerable operator attention and was consequently only operated routinely once a week at sunrise, and more frequently when DU personnel were on site for maintenance or for special campaigns. The spectral regions routinely covered were  $750\text{--}1250 \text{ cm}^{-1}$  and  $2400\text{--}3050 \text{ cm}^{-1}$ , and vertical column densities of  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{CHClF}_2$  were retrieved from the data. In August 1995, this system was replaced with a Bruker 120HR system. The new system includes a weather station and control software designed and fabricated at DU. It is almost completely automated, requiring an operator only to fill the detector dewars with liquid nitrogen, and runs twice daily when weather permits. With the installation of this instrument, additional spectral intervals were added, permitting the retrieval of column densities for additional molecules. In this study the trends for 12 molecules are presented, and  $\text{O}_3$  values measured with the FTS are compared with Dobson measurements for the 10-yr period of 1991–2000.

## RESULTS AND DISCUSSION

Shown here are the cumulative results of the observations: a 10-yr record for  $\text{O}_3$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{HCl}$ , and  $\text{CHClF}_2$  (HCFC-22), and a 6-yr record for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{HCN}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HF}$ , and  $\text{CO}$ .

The analysis was performed using the computer code SFIT [Rinsland *et al.*, 1984], which minimized the root mean square residual between a simulated spectrum and the observed spectrum by multiplying an assumed vertical volume mixing ratio profile by a scaling factor. The present analysis employed the HITRAN 96 spectral-line-parameter data base [Rothman *et al.*, 1998] and the pressure-temperature profiles from the daily National Weather Service radiosondes launched from Hilo, Hawaii.

A comparison was conducted between  $\text{O}_3$  measured with a Dobson [Dobson and Harrison, 1926; Dobson, 1957] and FTS measurements (Figure 1) (R. Van Allen *et al.*, unpublished manuscript, 2002). For this comparison points that were as close in time as possible were chosen, but always within 24 hours. For the 1991–1994 data, measured with a Bomem spectrometer, a systematic offset between FTS measurements and the Dobson was found. The Dobson data were taken from the World Ozone and Ultraviolet Data Centre (WOUDC). The ratio average (Dobson/FTS) for 1991–1992 is 1.03, with a standard deviation (SD) of 0.04, and for 1993–1994 the average ratio is 1.03, with a SD of

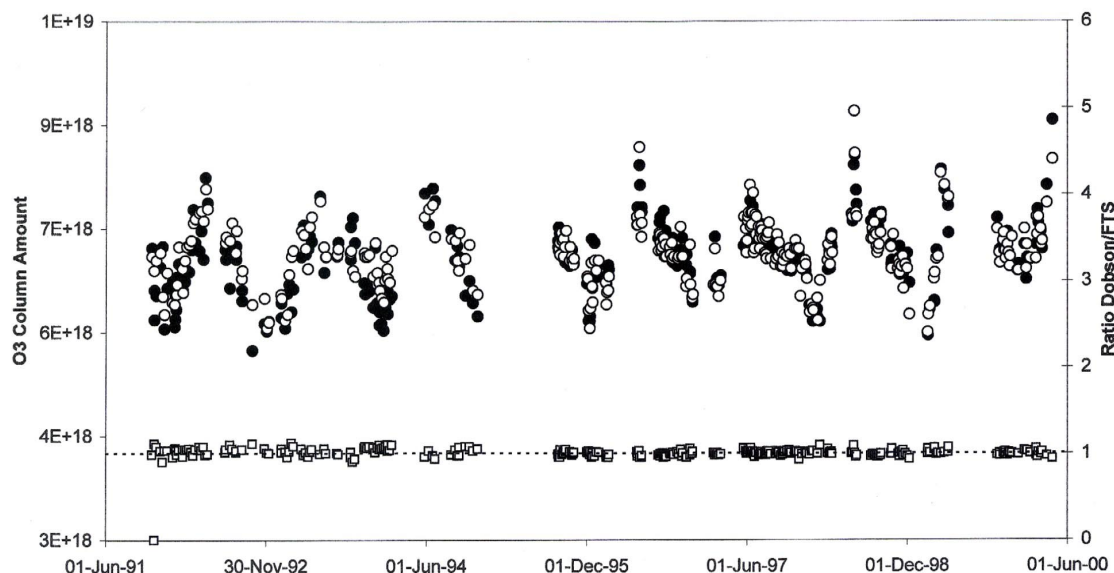


Fig. 1. Comparison between  $\text{O}_3$  retrieved with a Dobson (white circles) and with a FTS (black circles), at MLO. The ratio Dobson/FTS (open square) is also shown.

0.05. This comparison of the 1991-1992 data agrees well with previous studies [David *et al.*, 1993]. The small difference in the systematic offset between the current and the previous analysis is due to the fact that points were matched in the current comparison, while the previous study used averages. The agreement between Dobson and FTS

values is much improved for the Bruker data. The average ratio for 1995-2000 is 1.00, with a SD of 0.025.

The seasonal cycles of  $O_3$  and  $HNO_3$  are shown in Figure 2. Ozone amounts showed no obvious trend from 1991 to 2000. The recovery of  $HNO_3$  from Pinatubo-induced high levels is apparent from 1991 to 1996, with an overall

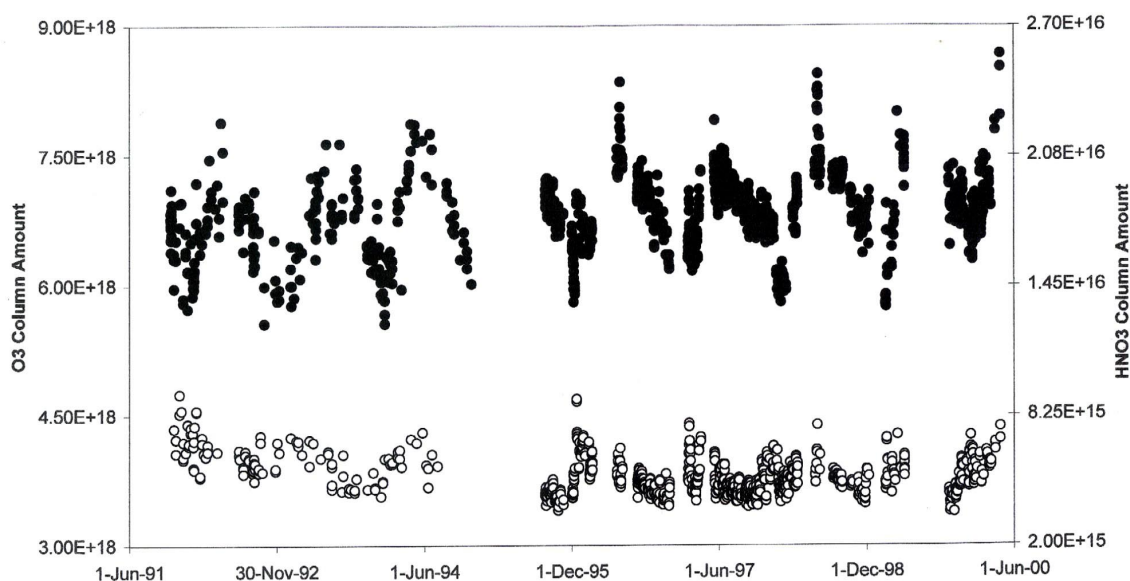


Fig. 2. Total column amounts of  $O_3$  (black circles) and  $HNO_3$  (white circles), at MLO.

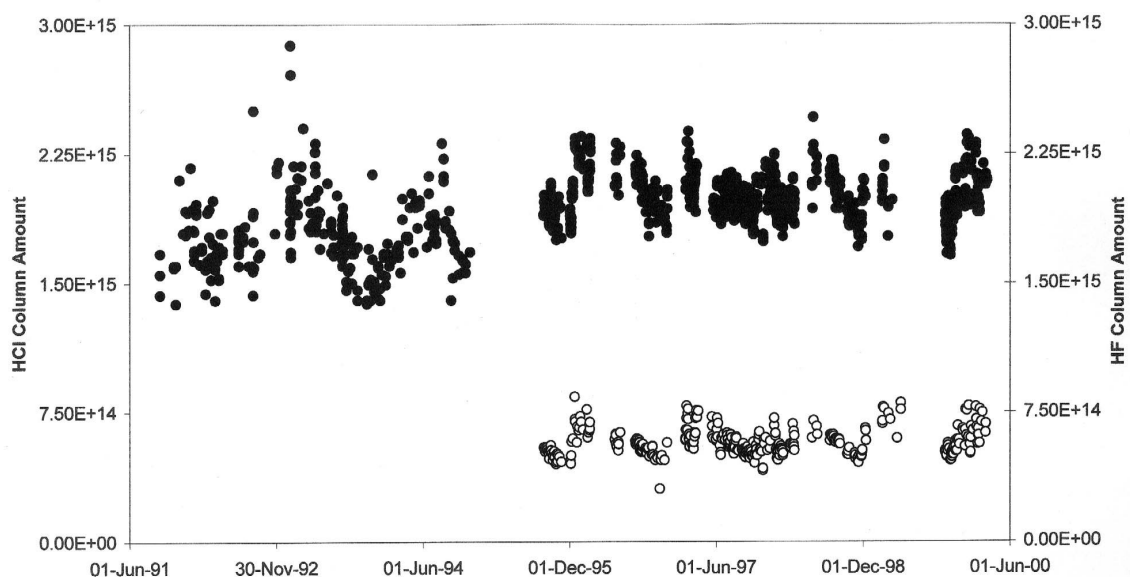


Fig. 3. Total column amounts of  $HCl$  (black circles) and  $HF$  (white circles), at MLO.

decrease of about 30%. During 1997-2001 there is no apparent trend in  $\text{HNO}_3$ .

The quasi-seasonal trend in  $\text{HCl}$  and  $\text{HF}$  is shown in Figure 3. The increase in  $\text{HF}$  is approximately 12% from 1995 to 2001. The increase in  $\text{HCl}$  for the same time period is about 6%.

Figure 4 shows the high variability of  $\text{CO}$ , and the overall increase in  $\text{HCFC-22}$  of about 50% between 1991 and 1998, where the trend levels off.

Figure 5 shows  $\text{C}_2\text{H}_6$  and  $\text{HCN}$ . The high values of  $\text{C}_2\text{H}_6$ ,  $\text{HCN}$ , and  $\text{CO}$  at the end of 1997 and in 1998 correlate with

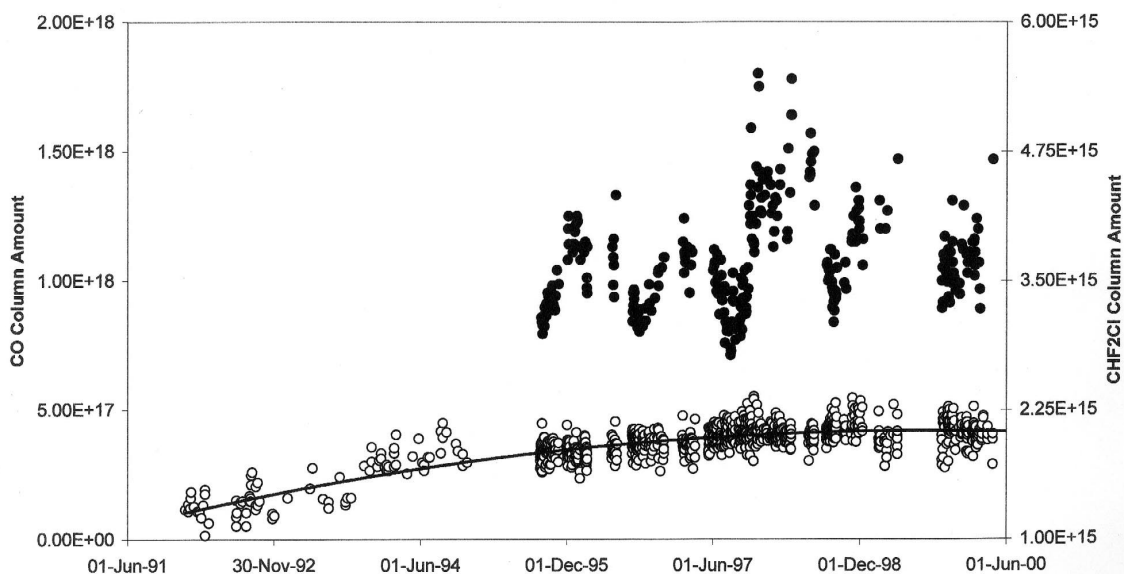


Fig. 4. Total column amounts of  $\text{HCFC-22}$  (white circles) and  $\text{CO}$  (black circles), at MLO. The polynomial fit (second order) shows that  $\text{HCFC-22}$  amounts level off in 1998.

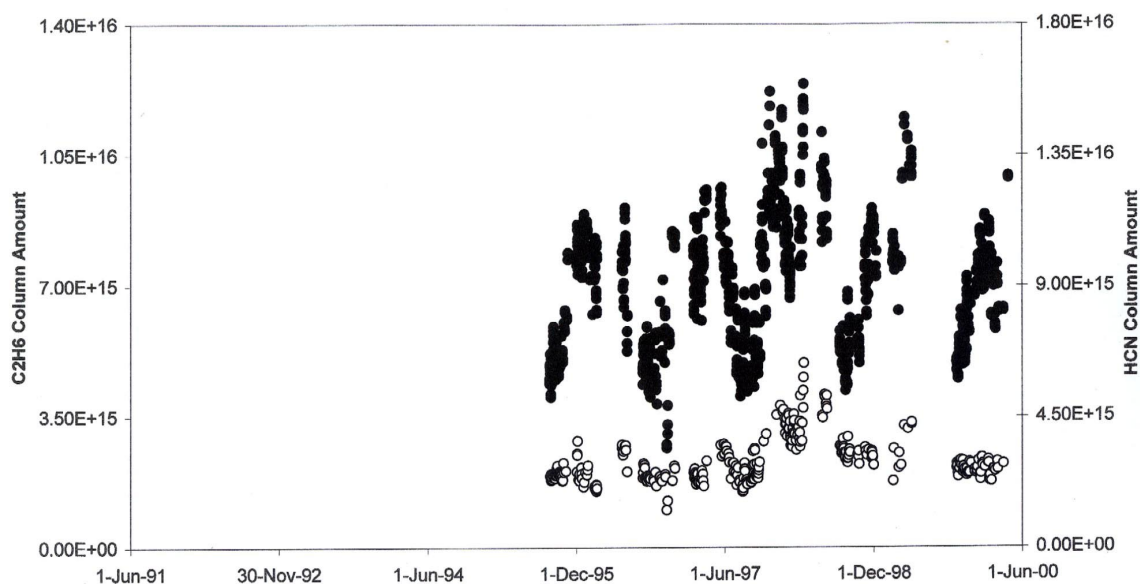


Fig. 5. Total column amounts of  $\text{C}_2\text{H}_6$  (black circles) and  $\text{HCN}$  (white circles), at MLO.

Asian tropical fires [Rinsland *et al.*, 1999]. Figure 6 shows NO and NO<sub>2</sub>. Photochemistry is evident in AM-PM differences.

Figure 7 shows CH<sub>4</sub> and N<sub>2</sub>O. No significant trends are observed, and the retrieval of these molecules can be used to study the achievable precision.

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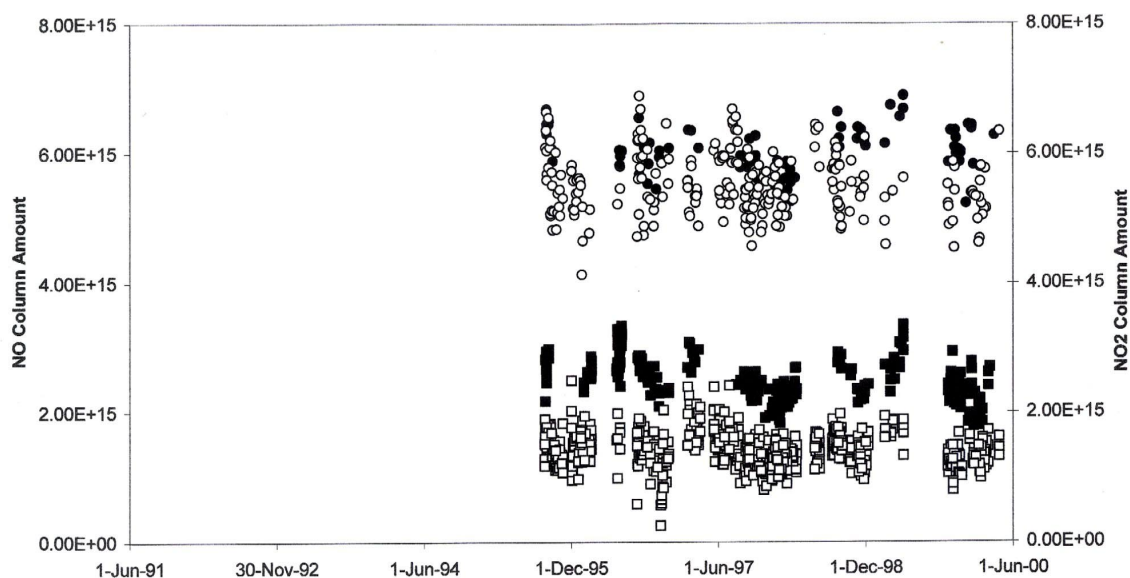


Fig. 6. Total column amounts of NO-sunset (black circles), NO-sunrise (white circles), NO<sub>2</sub>-sunset (black squares), and NO<sub>2</sub>-sunrise (white squares), at MLO.

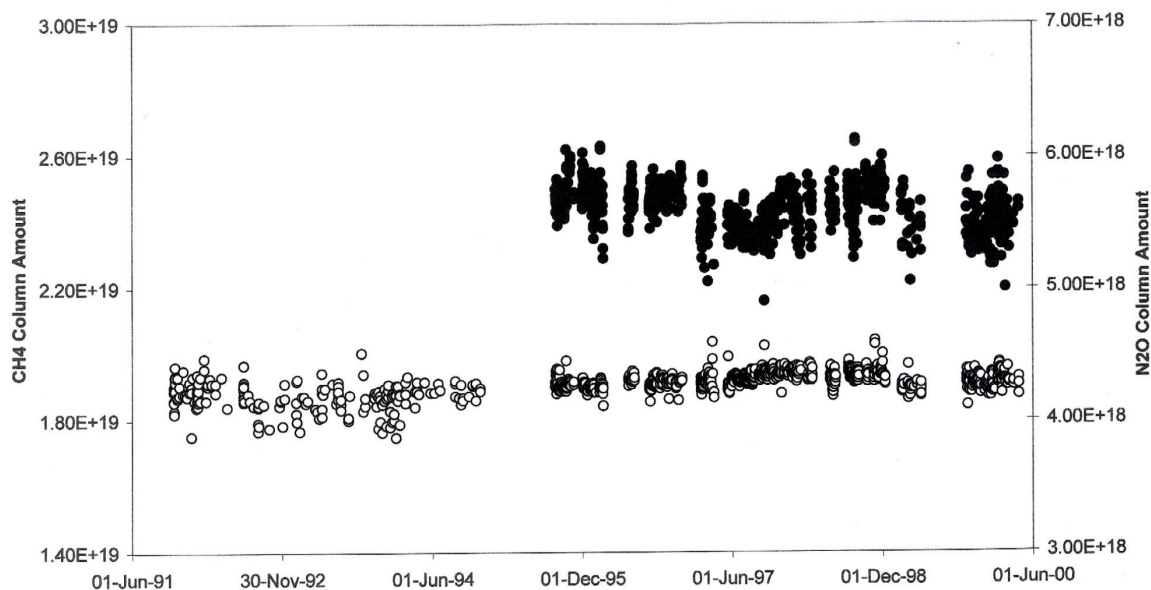


Fig. 7. Total column amounts of CH<sub>4</sub> (black circles) and N<sub>2</sub>O (white circles), at MLO.

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